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14. ABSTRACT We report on successful and unique design and implementation of highly expandable and compact photoelectron spectroscopy tools for in-situ characterization of complex functional superlattices and ultra-thin films. The analytical instruments are directly coupled with the PLD growth chamber. Our sample manipulator is designed for the sample transfer into either chamber. Initially, the prime set of tools allows for XPS, Auger and EELS spectroscopies.					
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## Report Title

Final Report: IN-SITU ANALYSIS SYSTEM FOR CORRELATED ELECTRON HETEROSTRUCTURES.

### ABSTRACT

We report on successful and unique design and implementation of highly expandable and compact photo-electron spectroscopy tools for in-situ characterization of complex functional superlattices and ultra-thin films. The analytical instruments are directly coupled with the PLD growth chamber. Our sample manipulator is designed for the sample transfer into either chamber. Initially, the prime set of tools allows for XPS, Auger and EELS spectroscopies.

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Gordon and Betty Moore Foundation award, 2014.

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<u>NAME</u>	<u>PERCENT SUPPORTED</u>	Discipline
Derek Meyers	0.00	
<b>FTE Equivalent:</b>	<b>0.00</b>	
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<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Michael Kareev	0.00
<b>FTE Equivalent:</b>	<b>0.00</b>
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**Total Number:**

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**Sub Contractors (DD882)**

## **Inventions (DD882)**

### **Scientific Progress**

See Attachment

### **Technology Transfer**

See Attachment

# DURIP FINAL REPORT - 'IN-SITU ANALYSIS SYSTEM FOR CORRELATED ELECTRON HETEROSTRUCTURES' /W911NF-11-1-0408/

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Comprehensive post-growth studies of artificial heterostructure based on complex oxides demand high vacuum requirements that are typical for surface analysis with semiconductor materials and elemental metals. Specifically, films must be pristine and ideally remain intact during analytical procedure [1]. In addition, to avoid hindering effects from the surface contamination a surface/interface subjected to investigation requires that adsorption from residual process gases does not generate an intolerable amount of *impurities* on the analyzed surface. Situation may become even worse in the case of exposure to ambient atmosphere. This issue brings to the forefront of the necessity of *in-situ* spectroscopic characterization tools to investigate ultra-thin films and heterostructures.

On the other hand, high-temperature growth conditions (typical for oxide materials) require strong coupling between the substrate and heating system. Thus, the problem of transferring of a synthesized sample from the PLD growth chamber into the analytical

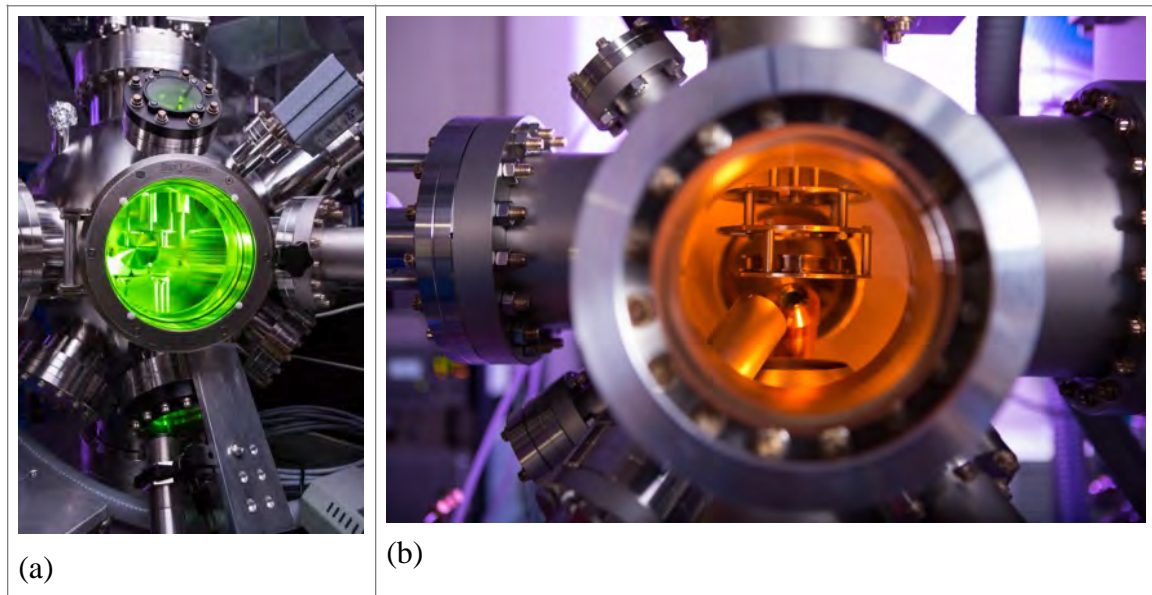


Figure 1. (a) An empty Neocera's sample holder rack/stage seen through the quick-entry door with a viewport in growth chamber. (b) The substrate carrier sitting on the lower plate of an identical rack at the center of the analytical chamber.

chamber involves a rather complex engineering design described below. A laser heater



(fiber-coupled, high-power 808 nm diode laser JOLD -100-CPXF-2P, Jenoptik), is free of such limitations because the substrate carrier (Neocera design) is decoupled from the heater and load-lockable. Figure 1a shows the empty Neocera's sample holder rack/stage as seen through the quick-entry door with a viewport in the center of the PLD chamber; Figure 1b demonstrates (via the quartz viewport) the substrate carrier sitting on the lower plate of an identical rack at the center of the analytical chamber (in partnership between UofA and STAIB) after the sample transfer.

Now carrier is placed in the position and ready for XPS analysis. In this geometry the first stage of CMA (DESA-150, STAIB Instruments) is on the bottom and the x-ray source (with small Al window) is translated closer to the sample.

## 1. TECHNICAL CHARACTERISTICS OF DESA-150.

### DOUBLE PASS, HIGH SENSITIVITY, HIGH RESOLUTION ENERGY ANALYZER DESA-150

Working distance	55 mm (standard)
Lateral acceptance area	2 mm diameter
Longitudinal acceptance depth	$\pm 3$ mm
Resolution guaranteed	$\Delta E/E$ 0.6% down to 0.05%
Resolution at 1000 eV, $\Delta E$	less than 1 eV on elastic peak
Resolution at 20 eV, $\Delta E$	less than 80 meV
Signal to noise ratio on silver	
Pulse counting	400:1 or better
Lock-in mode	600:1
Working modes	
Constant Energy Resolution	Yes
Constant Resolving Power	Yes
Energy resolution	Computer controlled from 0.05 to 6 eV
Energy range	0 eV to 2500 eV
Acceptance angle	6% of 2p (21.6°)
Detection	Channeltron type electron multiplier
Mounting flange	CF-150; minimum ID required
Flange-sample distance	8" and 10"
Shielding	$\mu$ metal
Bakeout temperature	250° C
Linear retraction (option)	Yes
Analyzer control	Model # NESA-2500
Integrated electron source	Model EK-5-IK
Beam energy	10 eV to 5 keV

Spot size	80 $\mu\text{m}$
Beam current	0.1nA up to 20 $\mu\text{A}$
Filament	Tungsten hairpin
Scanning plates	Yes
Source control	Model # NEK-315-S
Scan control (option)	Model # RG-TV 4
RQ-300-X2 XPS package	Dual anode (Mg/Al) 300 W x-ray source, Water- cooling circuit, 15kV Glassman high-voltage source 2" Z retraction for x-ray source;

#### DETECTION MODE OPTIONS

Lock-In mode	Yes
Pulse counting mode	Yes
Both modes	Yes

#### DATA ACQUISITION

WinSpectro-32 multitasking acquisition package for Windows (basic software) available with optional modules:

WinAES-32 for Auger Electron Spectroscopy

WinXPS-32 for XPS studies

WinUPS-32 for UPS studies

## 2. SAMPLE TRANSFER

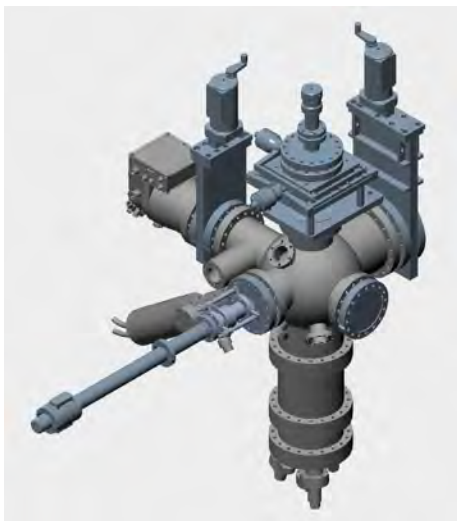


Figure 2. A schematic of the analytical chamber showing a X-Y manipulator and linear positioner on the top of the analytical chamber.

To transfer the sample carrier we use the custom designed system shown in Fig 2. The important part of the translation system is the combination of a X-Y manipulator (MC-2000-1.4, McAllister) with a long traveling range linear positioner (L-2231-6, Huntington Labs) sitting on the top of the analytical chamber. Linear translation along Z allows us to setup up the sample holder in to different positions for analysis/alignment and translation of the carrier. The positioning magnetic transporter (VF-6195-36-GR, Huntington Labs) with a port aligner (Pfeiffer) is shown in the left low corner of Fig. 2. Special non-slide design of fork (U of A) allows the safe transfer of substrate carrier between chambers.

Figure 3 provides a comprehensive view of the experimental setup after all tuning and calibration procedures. For proper translation it is necessary to equalize the pressure difference between the PLD growth chamber (typically  $5\text{--}7 \times 10^{-8}$  Torr) and the analytical chamber (typically  $3\text{--}5 \times 10^{-9}$  Torr) by using an 8" gate valve (VAT) to connect both chambers directly (shown at the center in Fig 3).

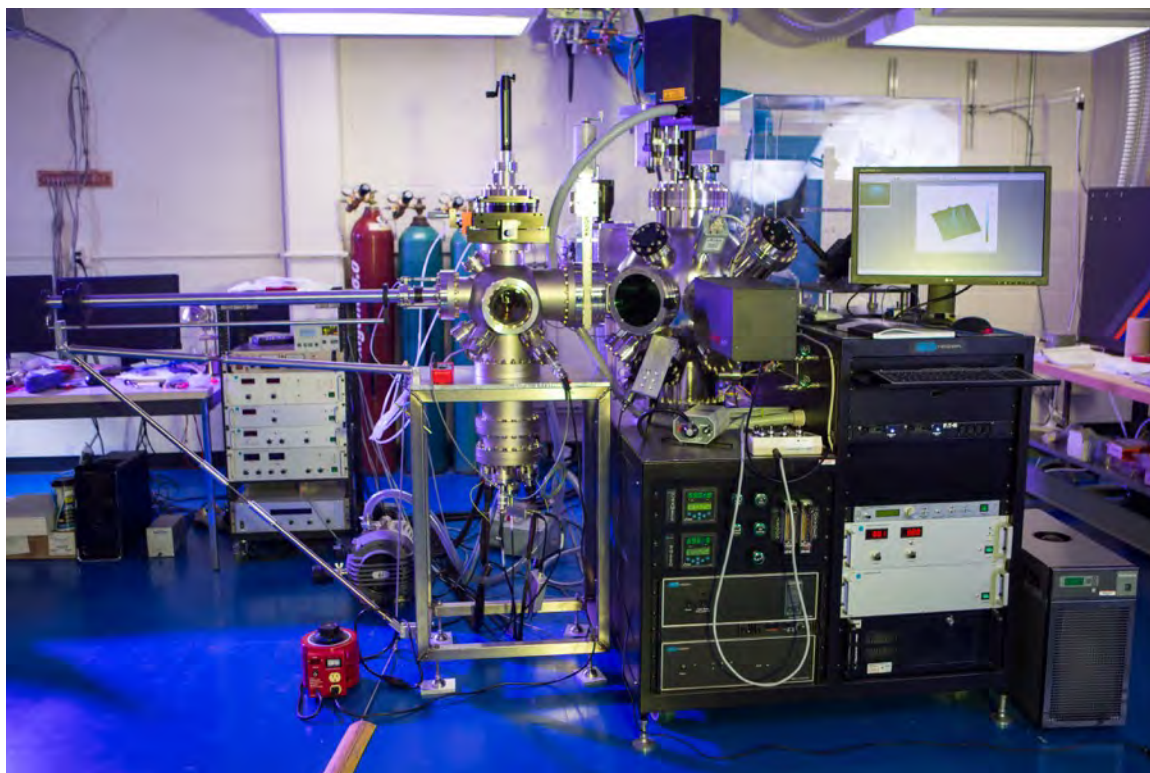


Figure 3. *A general view of the growth and analytical chambers after commissioning in 2013-14 ready for measurements.*

### 3. SELECTED EXAMPLES OF XPS/AUGER/EELS PERFORMANCE.

The importance of a clean surface condition for proper analysis was already mentioned above. Figure 4 shows a survey spectrum of  $\text{SrTiO}_3$  single-crystal and confirms that our design indeed satisfies those vitally important requirements. Note, the surface shown in Fig. 4 was subjected to the special thermal treatment at high temperature, i.e. cleaning *in vacuum*. As seen the contamination from residual process gas atmosphere is absent. Meanwhile the peaks from the main chemical constituents, i.e. Sr, Ti, and O are clearly distinguishable along with a small trace of La impurities typically present in this

compound. Because of limited space inside the analytical chamber, a non-monochromatic X-ray source with Al and Mg anodes were used. In addition, the X-ray excited Auger transition peaks are clearly observed as well.

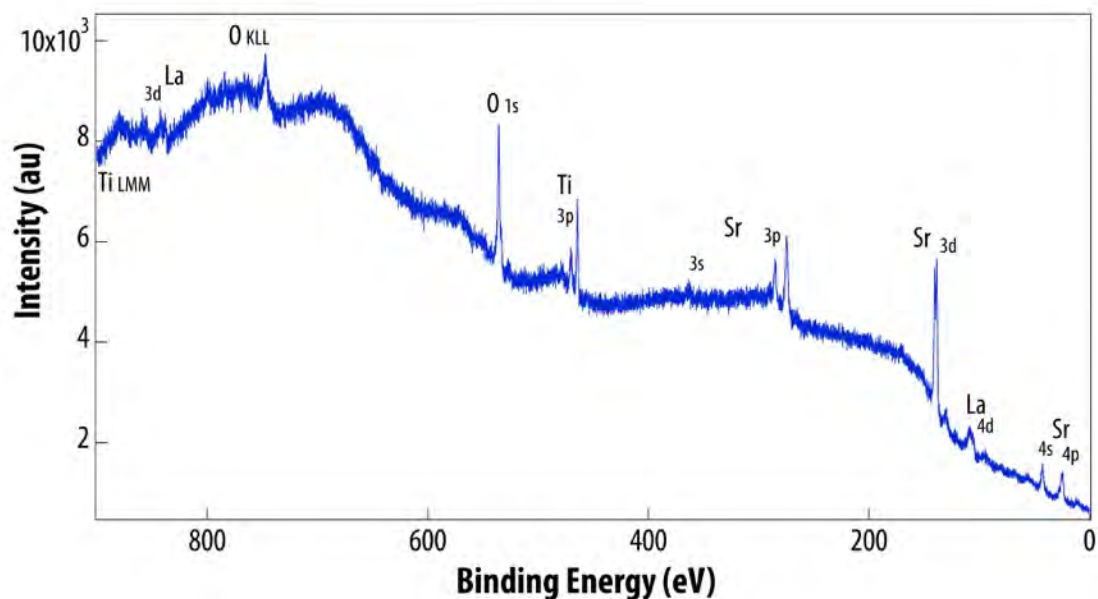


Figure 4. *Example of a survey scan of the SrTiO<sub>3</sub> single crystal substrate, after surface cleaning via annealing in vacuum. Details are given in the main text.*

First results from the usage of this analytical instruments has been reported in Ref . 2 and 3. Apart from XPS results figures 5 and 6 demonstrates the Auger- and EEL spectroscopies integrated into the very same machine.

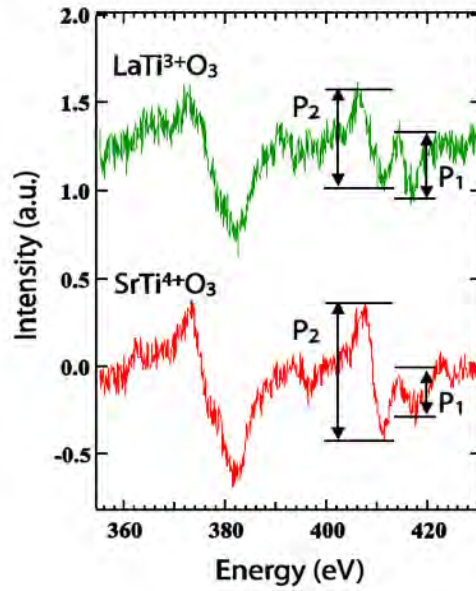


Figure 5. XPS excited Auger spectra which allows to determine the charge states of Ti. Specifically, the ratio of  $P_1/P_2$  is sensitive to the valence state of Ti which can be used to distinguish between  $Ti^{3+}$  and  $Ti^{4+}$ .

#### 4. FURTHER DIRECTIONS AND OPERATIONAL MODES.

Recently (spring-summer 2014), we have initiated further development of new characterization methods to incorporate into the existing setup. En route to this goal, we have addressed the crucial issue of decoupling the sample carrier from the electrical ground. For instance, the experimental arrangement used for total current (TC) spectra studies is now highly compatible with our XPS/AES-EELS setup. In this mode, the Cylindrical Mirror Analyzer (CMA) allows us to measure, along with total current spectroscopy (recorded in the sample circuit), the spectra of the *reflected current* – both total and elastically reflected. Thus, it is now possible to investigate the surface not only by typical yield methods (TCS) but also by the *secondary electron energy-resolved methods* (such as commonly

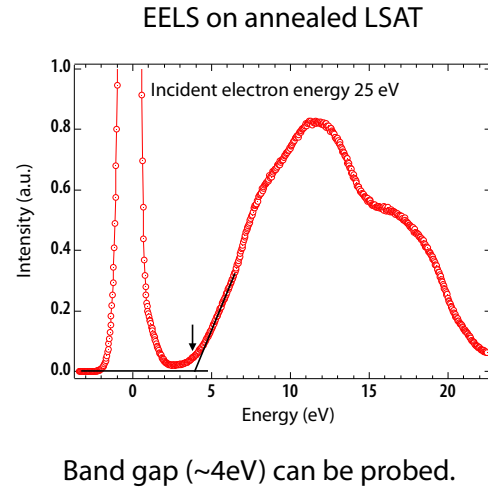


Figure 6. An example of a new measurement mode, i.e. the EELS mode which allows to determine a band gap of films. In this specific case we used LSAT single crystal with the band gap of 4 eV.

known AES and EELS or even by more exotic Appearance/Disappearance spectroscopy). We note, this opens up exciting opportunities since the TCS is a very sensitive method for the investigation of both density of valence and empty states in the near surface region of complex oxides in the energy interval 10-15 eV relative to the Fermi level.

#### References

1. Siegfried Hofmann, *Auger- and X-Ray Photoelectron Spectroscopy in Material Science: A User Guide*, Springer Series in Surface Sciences 49, 2013.
2. “*Electronic and magnetic properties of (111)-oriented CoCr<sub>2</sub>O<sub>4</sub> epitaxial thin film*”  
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